

Sources and Reduction of SO₂-Emissions

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Summary:

The SO₂ emission of a cement plant depends on the

- ◆ type of the kiln
- ◆ quality of the raw material and fuel
- ◆ operating conditions of the kiln and the raw mill system
- ◆ secondary SO₂ reduction measures

To reduce the SO₂ emission from a pyroprocessing system, three basically different methods are available:

- ◆ Maintain the existing process while reducing the sulfur input into the system
- ◆ Modify the existing process (primary reduction measures)
- ◆ Maintain the existing process while adding a separate gas cleaning unit for the exhaust gas (secondary reduction measures)

With today's technology it is possible to reduce the SO₂ emission to an acceptable level. The main methods are SO₂ absorption with Ca(OH)₂ in the preheater or in a separate scrubber and adjustments of the raw material.

1. INTRODUCTION

SO₂ was one of the first air pollutant with which the public made very negative experiences. Mainly SO₂ but also other pollutants from coal fires in the city of London were responsible for the death of 4000 people between December 5 and 9, 1952.

Today, the SO₂ emission is known to be responsible for a part of the acid rain which is attacking plants and animals, for increased pH of lakes and for corrosion and decomposition of buildings.

Today, the total worldwide SO₂ emission is declining because of reduced sulfur content in the fuels and scrubbers for large SO₂ sources like coal or fuel fired power stations.

The SO₂ emission of some cement plants is still on the high side and should be reduced in the future. The formation of SO₂ in kiln systems and methods to reduce them are presented hereafter.

2. CHEMICAL AND PHYSICAL PROPERTIES AND ENVIRONMENTAL ASPECTS OF SOME SULFUR COMPOUNDS

Sulfur (S)

Sulfur is the 15th most common terrestrial element and the 9th most abundant element in the universe. It is widely distributed in nature in different compounds as well as in pure form. The main sulfur content of the lithosphere is estimated to be approx. 0.05%.

Physical Properties [1]

The melting / solidification point of normal sulfur is 119.3 - 114.5°C, depending on the mode of heating.

Density of solid at 20°C, kg/m³

Rhombic α 2070

Melting point, °C, Natural

Rhombic α 110.2

Density of liquid, kg/m³

115°C 1808

445°C 1614

Boiling point, °C 444.6

Density of vapor /

density of air, 470°C 1.837

Chemical Properties

Molecular weight: 32,1 g/mol

Sulfur is one of the most reactive elements; it reacts directly with most elements except iodine, gold, platinum and the noble gases. In humid air it is weakly oxidized, forming traces of sulfur dioxide and sulfurous acid. At approx. 250°C, sulfur ignites in air and burns with a blue flame but the presence of sulfur dioxide significantly raises the ignition point.

Pyrite / Marcasite (FeS₂)

Common and important iron and sulfur mineral

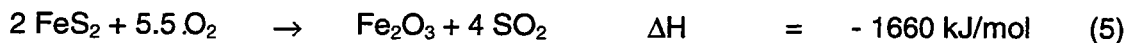
Physical Properties [13], [2]

	Pyrite	Marcasite
Cristalline form	cub.	rhomb.
Density t/m ³	5	4.87
Melting point °C	1'171	450
Solvent	HNO ₃	HNO ₃

Chemical Properties [2]

	Pyrite	Marcasite
Molecular weight g/mol	119.98	119.98
Ignition temperature °C	350 - 550	
Complete combustion °C	850 - 940	

Four main reaction steps (Eqs. 3 - 6) make up the overall pyrite roasting reaction (represented by Eq. 7). The specified enthalpy values [7] refer to 298 K:



Sulfur Dioxide (SO₂)

Sulfur dioxide is produced industrially in greater quantities than any other single sulfur compound. It is generated as the first stage in the manufacture of virtually all the sulfuric acid used by industry, irrespective of the basic raw material.

Physical Properties [1]

Sulfur dioxide, SO₂, is a colorless, non-flammable, toxic gas with a characteristic pungent smell and acid taste.

Melting point (101.3 kPa)	- 75.5°C
Dynamic viscosity at 0°C	368 Pas
Critical temperature	157.5°C
Boiling point (101.3 kPa)	- 10.0°C
Latent heat of vaporization (at <i>bp</i>)	402 J/g
Standard density at 0°C (101.3 kPa)	2.93 kg/m ³
Standard enthalpy of formation	- 4636 J/g

Specific heat capacity c_p (101.3 kPa):

0°C 586 J kg⁻¹ K⁻¹

500°C 816 J kg⁻¹ K⁻¹

Chemical Properties [1]

Molecular weight: 64.06 g/mol

Sulfur dioxide is very stable; thermal dissociation becomes significant only above 2'000°C. It can be decomposed by shock waves, irradiation with ultraviolet or X rays or by electric discharge.

The reaction of sulfur dioxide with oxygen to form sulfur trioxide is industrially the most significant of all its reactions because of its importance in sulfuric acid production. In the gas phase, it only takes place at elevated temperatures and, for a satisfactory yield of sulfur trioxide, it requires the presence of a catalyst. In aqueous solution, sulfur dioxide is oxidized to sulfuric acid at low temperature by air in the presence of activated coke or nitrous gases, or by oxidizing agents such as hydrogen peroxide.

Environmental Aspects and Toxicology [1]

A substantially larger amount of sulfur dioxide than utilized industrially is produced by the combustion of sulfurous fossil fuels and is discharged into the atmosphere with the flue gases. The calculated total emission of sulfur dioxide from power stations, traffic, households, industry and trade in the Federal Republic of Germany in 1975 amounted to approx. 3.6×10^6 t. In contrast, only about 2.7×10^6 were used for that year's sulfuric acid production of approx. 4.2×10^6 t H_2SO_4 .

In the last years the SO_2 emissions from power plants in Germany were reduced continuously with the installation of flue gas desulfurization plant and with the utilization of low-sulfur fuels, but emissions from traffic, households, industry, etc. in 1990 still account for 620×10^3 t/a. Emissions from power stations amounted to 320×10^3 t/a.

For worldwide atmospheric emissions, only rough estimates are available. For 1970, while global emissions were estimated at 157×10^6 t SO_2 , only about 61×10^6 t were consumed in the production of approx. 94×10^6 t of sulfuric acid. The worldwide cement production (1985) is estimated to about 700×10^6 t/a. Based on an average SO_2 concentration of about 1000 mg/Nm^3 , the portion of SO_2 emitted by cement plants compared to the total anthropogenic SO_2 emission (200×10^6 t/a) is about 0.7% [5].

Large-scale emission of sulfur dioxide close to ground level has indisputably been the cause of some spectacular environmental problems in the past. A large area around Sudbury, Ontario, was completely sterilized by sulfur dioxide from primitive ore roasting operations around the turn of the century and much of it is still barren as a result of the ensuing soil erosion. Calamitous sulfuric acid fogs occurred in Donora, Pennsylvania, and London, England, in 1948 and 1952, when adverse climatic conditions prevented sulfur dioxide from industrial sources and domestic coal fires from dispersing.

The causes of these episodes were correctly identified and the action taken to control **ground level smoke** and sulfur dioxide concentrations has effectively prevented them from recurring. In the case of industrial sources, however, this has often been achieved by merely building taller chimneys to disperse the sulfur dioxide over a wider area and as the consumption of fuels has increased over the years it has been argued that the problem has merely been shifted from the location where the sulfur dioxide is produced to other locations downwind.

Considerable publicity has been given to the apparently increasing problem of **acid rain** and there does, indeed, seem to be a correlation between the incidence of acid rainfall and the atmospheric transport of pollutants from major industrial locations.

Establishing in any degree of certainty to what extent sulfur emissions are responsible for acid rain is, however, complicated by incomplete knowledge of the magnitude of sulfur emissions from natural sources, the atmospheric chemistry of sulfur and the importance of other potential acidulants such as nitrogen oxides.

Nevertheless, the evidence linking sulfur dioxide pollution to acid precipitation has been mounting gradually. A recent report by the U.S. National Academy of Sciences, for example, has stated that there appears to be a direct proportionate relationship between sulfur dioxide pollution and the amount of acidic sulfates in precipitation.

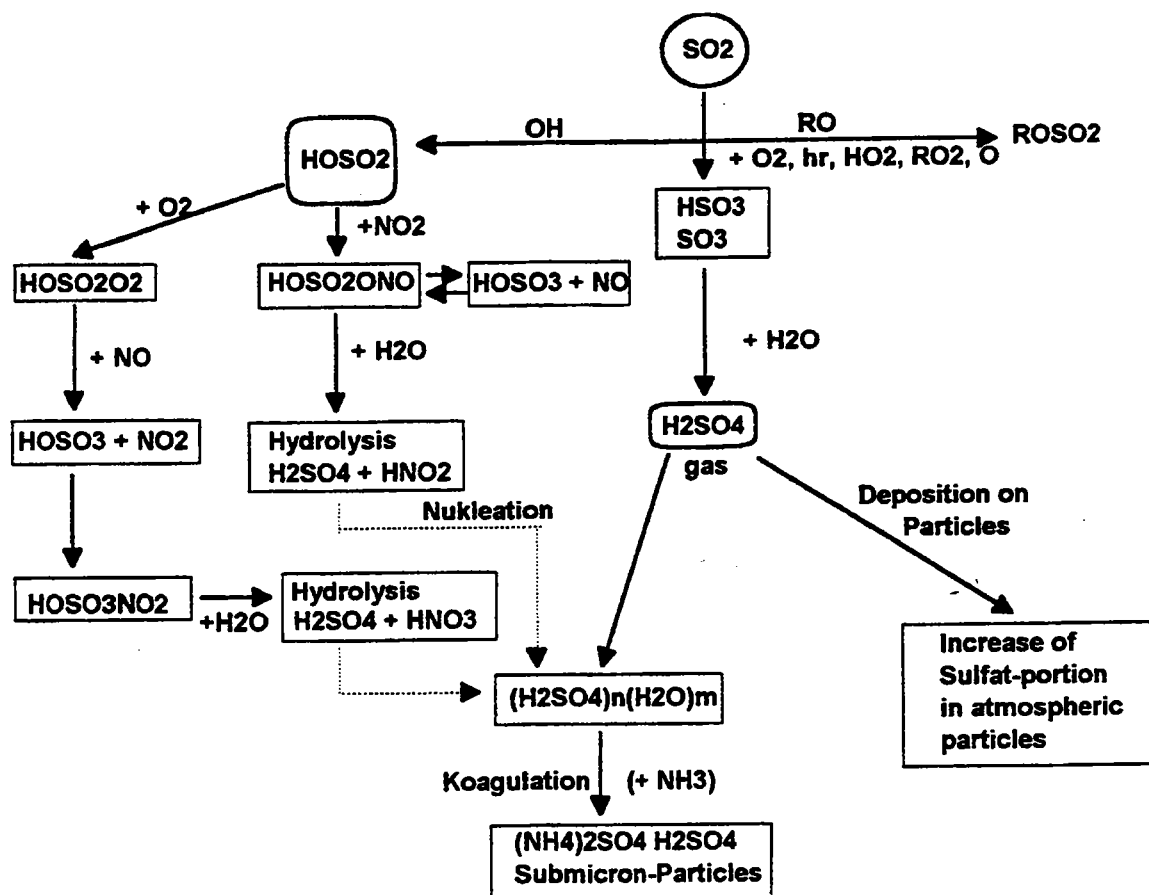
III-effects of sulfur dioxide on humans and animals are mainly related to irritation and damage of the moist mucous membranes by the formation of sulfurous acid. The odor threshold of sulfur dioxide in air is between 0.3 and 2.5 ppm. In most human beings, concentrations of 5 - 10 ppm will lead to irritation of the respiratory tract; in sensitive people they may produce spasms of the bronchi. Higher concentrations will cause heavy irritative coughing, while breathing sulfur dioxide at concentrations above 400 - 500 ppm, even for only a few minutes, is dangerous to life. The maximum workplace concentration is defined as 5 ppm (14 mg/m^3).

Long-term exposure may possible lead to bronchopneumonia and, in extreme cases, to toxic pulmonary edema with dyspnoea, cyanosis and cardiac-circulatory failure.

Sulfurous acid absorbed by the body is converted to sulfate and discharged in the urine, as evidenced by an increase in urine acidity.

Plants are impaired by sulfur dioxide at even lower concentrations than human beings. Sulfur dioxide levels of 1 - 2 ppm are enough to cause acute damage to the leaves of plants in only a few hours, followed by necrosis, probably resulting from impaired photosynthesis.

Atmospheric Chemistry of SO_2 [3]



Sulfuric Acid

Physical Properties

Pure sulfuric acid H_2SO_4 is a colorless, water-white, slightly viscous liquid, *mp* 10.4 C, *bp* 279.6°C. It can be mixed with water in any ratio.

Chemical Properties

Molecular weight: 98.08 g/mol

Sulfuric acid is a strong acid with characteristic hygroscopic and oxidizing properties. Sulfuric acid, like the sulfate ion, is chemically and thermally very stable.



Environmental Aspects and Toxicology [1]

Sulfuric acid has a highly corrosive effect on the eyes, the mucous membranes and the skin, even in low concentrations. Because it completely destroys living tissue, concentrated sulfuric acid causes burns that penetrate deeply and heal only slowly. Swallowing sulfuric acid produces extreme pain in the digestive tract, vomiting and shock and there is a danger of perforation.

Sulfuric acid vapors or mists irritate the eyes and the mucous membranes of the nose, pharynx and respiratory tract, causing heavy coughing and breathlessness.

Sulfuric acid releases are highly deleterious with respect to ground and surface waters. The substance is toxic to both fish and algae, both directly and as a result of reaction with other materials in the water. Any concentration $\geq 1.2 \text{ mg/L}$ is considered lethal to fish: 6.3 mg/L or more causes death within 24 h.

Sulfur Trioxide (SO₂)

Physical Properties

Gaseous SO_3

Nominal density, g/L (0°C, 1013 mbar) 3.57

Specific heat C_p , kJ $\text{m}^{-3} \text{K}^{-1}$

100°C 2.543

500°C 3.191

Liquid SO_3

Density, g/cm³ (25°C) 1.9

bp, °C (1013 mbar) 44.8

Heat of evaporation (boiling point), J/g 538

Vapor pressure, bar

20°C 0.26

100°C 8

Critical temperature, °C 217.7

3. SO₂ EMISSION LIMITS / NORMAL EMISSION

Emission Limits

Germany	400 mg/Nm ³ dry (no waste fuels)
Switzerland	500 mg/Nm ³ dry
Europe	100 - 2400 mg/Nm ³

Normal Emission

There is no normal SO₂ emission level for cement kilns. The SO₂ emission depends mainly on quantity and quality of "S" input, kiln system and SO₂ reduction systems. It is known that SO₂ emission of cement kilns can be between very low values of less than 50 mg/Nm³ and very high values up to 3500 mg/Nm³.

Figure 1 **Average SO₂ Emission according to a "Holderbank" Survey**

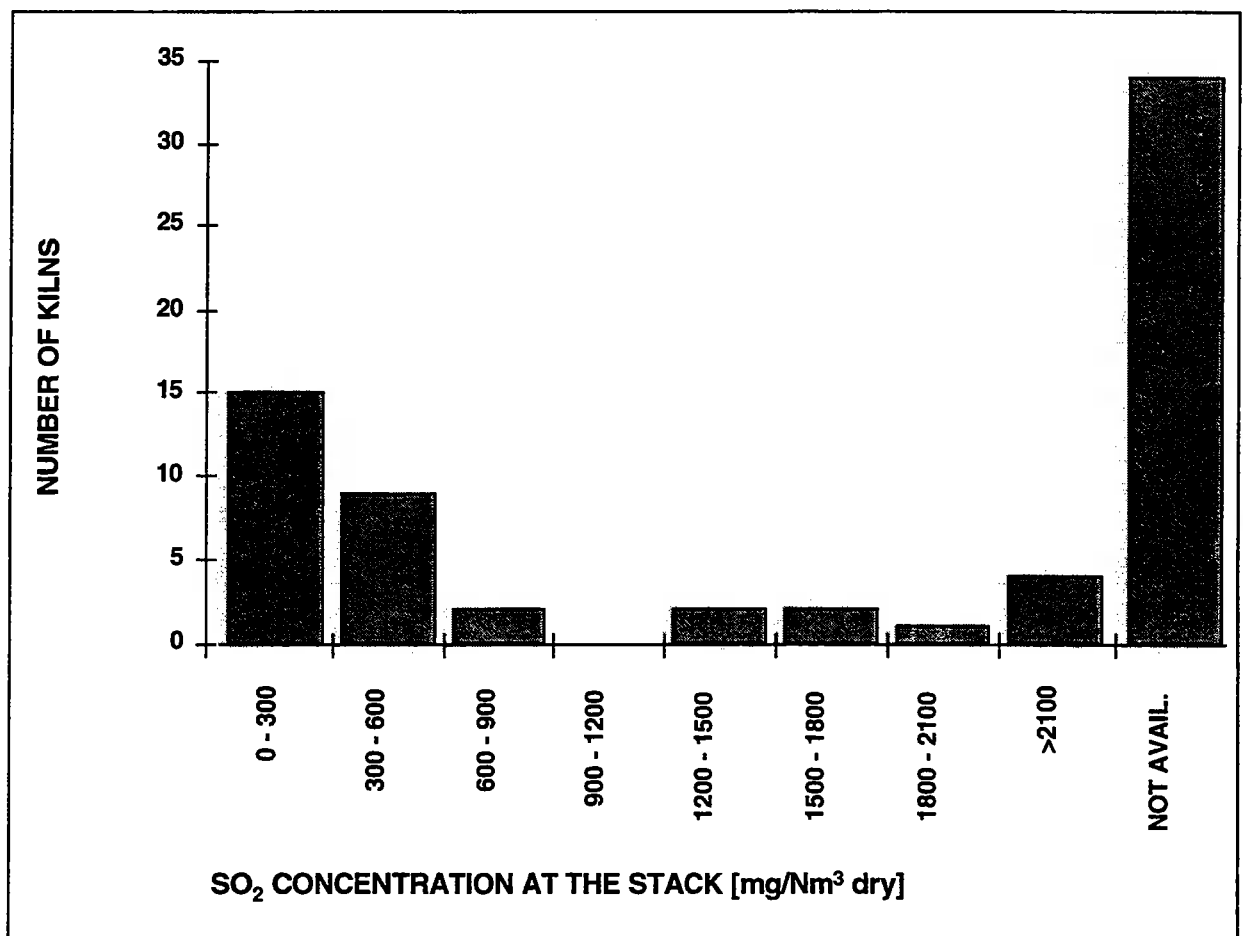
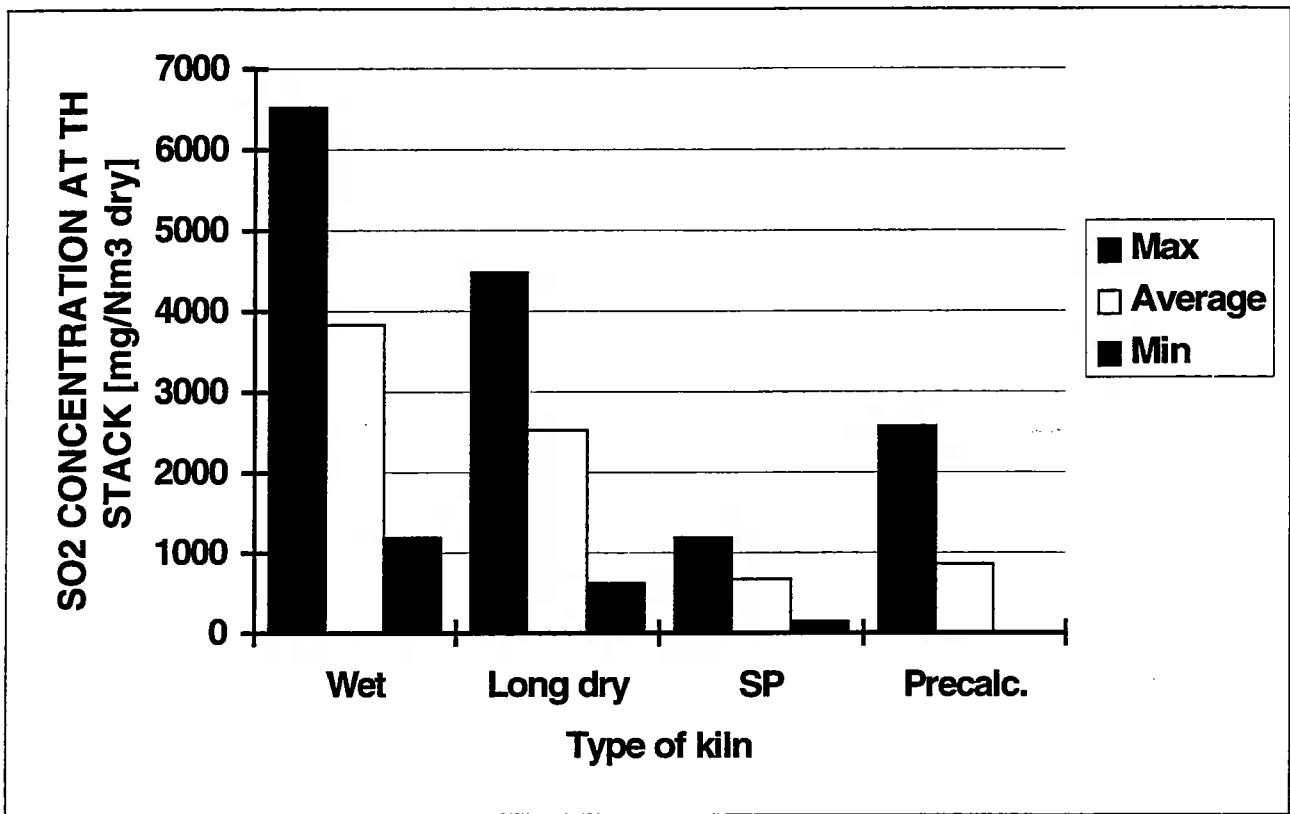


Figure 2 Result of PCA SO₂ emission survey 1982 [4]



Assumption: wet: 2.1 Nm³ dry / kg cli (18 kilns)
long dry: 1.5 Nm³ dry / kg cli (12 kilns)
SP: 1.4 Nm³ dry / kg cli (5 kilns)
Precalciner: 1.4 Nm³ dry / kg cli (12 kilns)

4. **SULFUR INPUT INTO KILN SYSTEM [4] [6]**

Contained in the raw materials (mainly as FeS_2) and the fuel, sulfur enters the process mainly in the form of sulfates (gypsum $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$), sulfides (Pyrit: FeS_2) and organic sulfur compounds. In the process, the sulfur compounds may either be reduced or oxidized to form gaseous SO_2 .

Table 1: Sulfur content of kiln feed and fuels of the "Holderbank" Plants in 1994

	% SO_3		
	Average	Minimum	Maximum
Kiln Feed	0.46	0	1.93
	% S		
	Average	Minimum	Maximum
Fuels			
Coal	0.86	0.02	3.51
Pet Coke	4.22	1.01	8.3
Diesel Oil	2.61	0.02	3.5
Heavy Fuel Oil	2.86	0.12	11.6
Alternative Fuels	Average	Minimum	Maximum
Liquid	0.56	0.11	2.01
Solid	0.92	0	3.9
Natural Gas	0.52	0	3.17
Tires	1.63	0.8	3.9
Waste Oil	1.16	0.5	2

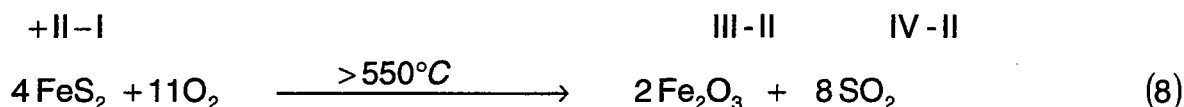
5. BEHAVIOR OF S-COMPOUNDS IN THE PROCESS

Wet Kilns

A schematic representation of the sulfur circulation in a wet kiln is shown in fig. 3. Depending on the raw materials, the conditions in the kiln burning zone and the internal circulation, 30 - 80% of the sulfate compounds entering the kiln burning zone may decompose and form SO₂ which leaves the kiln burning zone with the exhaust gas together with the SO₂ formed by oxidation of the organic sulfur in the fuel fired into the kiln.

On passing through the calcining zone, the preheating and the drying sections of the kiln, some of the SO₂ will be reabsorbed in the raw materials but due to the poor contact between the kiln gases and the raw materials, especially in the calcining zone, 40 - 60% of the SO₂ from the kiln burning zone will be emitted from the kiln.

In the preheating section of the kiln, the SO₂ concentration in the gas may even be increased if the raw materials contain sulfides which will burn here in accordance with equation:



Having left the kiln, the exhaust gas usually only passes through a precipitator before being emitted to the atmosphere through the stack.

Depending on the type of precipitator between 10 and 30% of the SO₂ in the exhaust gas may be absorbed in the raw materials at this stage. Taking into account internal circulation and the evaporation and absorption rates mentioned, about 30% of the sulfur entering the kiln system will be emitted as SO₂. The emission will increase roughly in proportion to the total input of sulfur compounds in raw materials and fuel.

Since the specific heat consumption of wet kilns is high, SO₂ emission depends very much on the sulfur content in the fuel. If the excess air is reduced below a certain level, a sharp rise in SO₂ emission from the kiln may occur, as local reducing conditions will increase SO₂ formation in the burning zone and make SO₂ reabsorption in the kiln back-end more difficult.

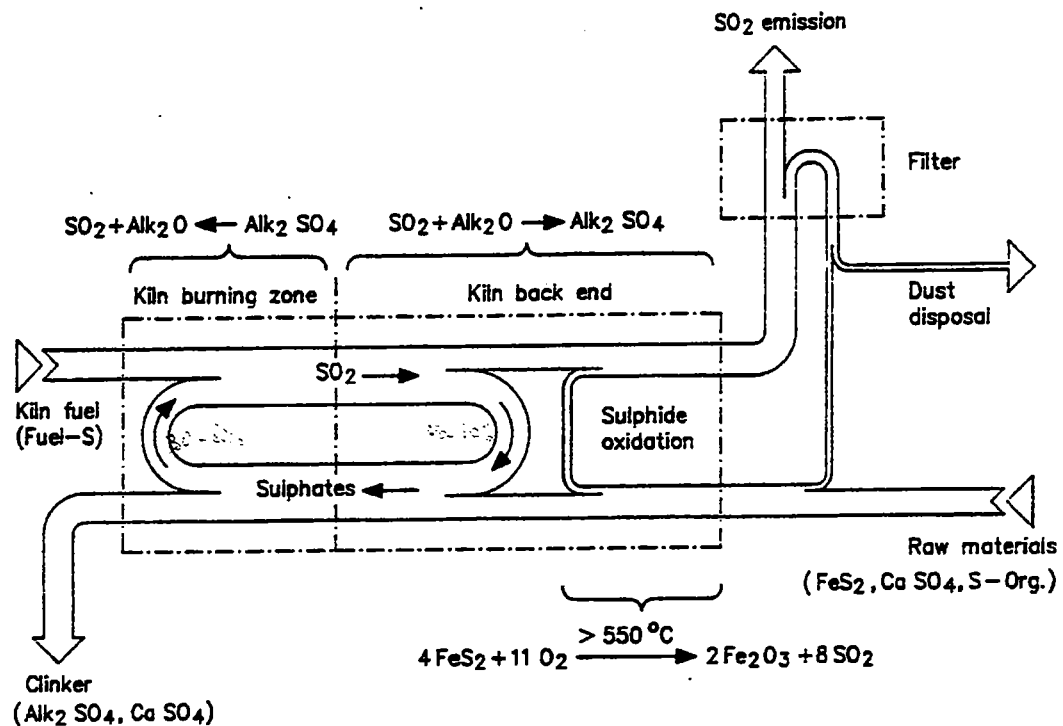
Long dry kilns

Except for a possible slurry preheating section, the design of the long dry kiln is virtually the same as that of a wet kiln.

Consequently, the SO₂ absorption factors are comparable to those of wet kilns as mentioned above.

However, with the same type of raw material and fuel the SO₂ emission from the long dry kiln system will be lower than that from the wet kiln. This is due to the lower specific heat consumption and the fact that the exhaust gases from the long dry kiln are often used for drying in the raw mill in which 20% - 50% of the SO₂ might be absorbed by intimate contact with freshly ground raw meal particles.

Figure 3 Behavior of sulfur in a wet or long dry kiln system without raw mill

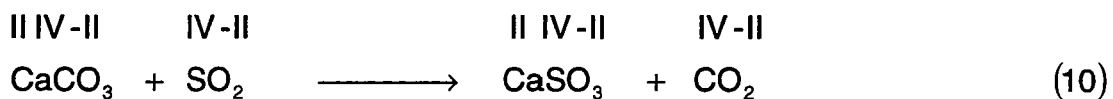
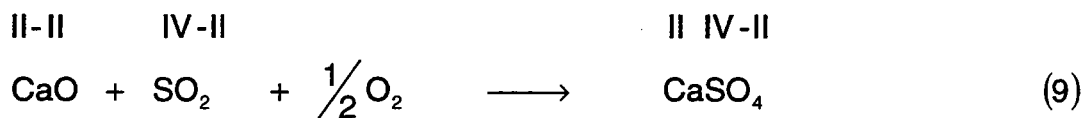


Preheater kilns

A schematic representation of the sulfur circulation in a dry-process preheater or precalciner kiln with bypass is shown in fig. 4.

In 4 and 5-stage cyclone preheater kilns complete preheating of the raw meal takes place in intimate contact with the exhaust gas from the kiln and in the lower stages the temperature reaches 850°C at which point part of the raw meal starts to calcine.

The SO₂ coming from the kiln is thus brought into contact with free CaO and CaCO₃ at a temperature at which the following reactions proceed relatively fast:



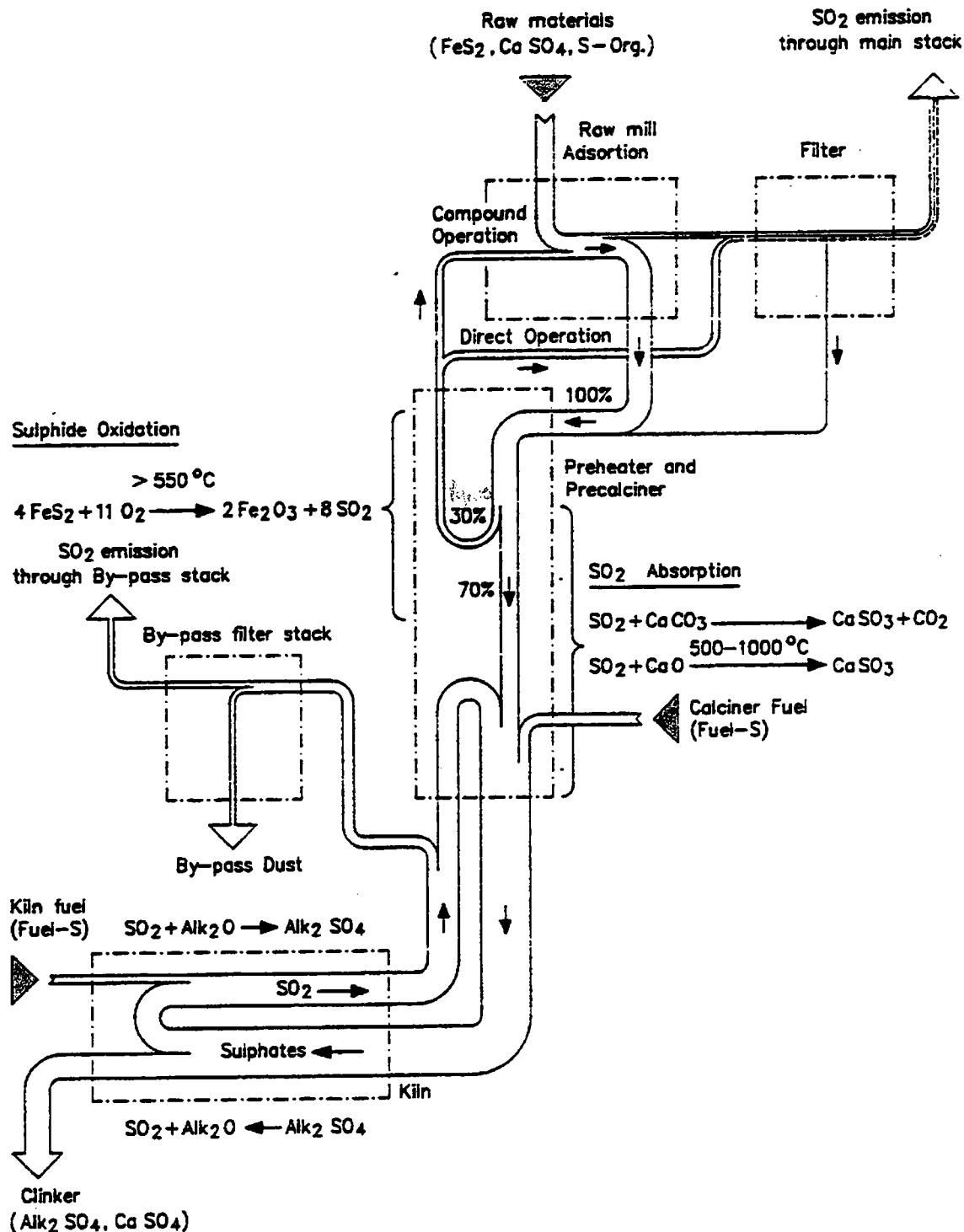
In this way, nearly all SO₂ formed in the kiln is absorbed by the hot meal and reintroduced into the kiln and bound into the clinker. Only if the sulfur circulation between the kiln and the lower preheater stage reaches extreme levels or in the case of local reducing condition in the kiln back-end and the riser duct SO₂ may escape via the lower stage. This will often be the case if coarse waste fuel (e.g. rubber tires or pieces) is fired into the riser duct or kiln inlet.

Except for this situation, considerable SO₂ emission from preheater kilns (without by-pass) will only occur in case the raw materials contain non-sulfates such as pyrites which form SO₂ already in the upper stage cyclones where the temperature and the concentration of free lime and alkaline materials are too low to ensure complete reabsorption of the SO₂ formed, according to above two reactions (9, 10).

Normally, 30 - 50% of the sulfur present in the raw meal in the form of pyrites will leave the preheater as SO₂. Part of this is absorbed in the raw mill and the precipitator. Still, SO₂ emission from the stack will amount to 15 - 30% of the sulfur entering with the raw materials in the form of non-sulfates.

This means an SO₂ emission of 500 - 1000 mg / kg cli for each per mil sulfur present as non-sulfate in the raw materials.

Figure 4 Behavior of sulfur in a preheater kiln system



Precalciner kilns

The precalciner kiln system in which the kiln gases pass the precalciner offers ideal conditions for absorption of SO_2 from the kiln due to the high amount of free CaO and a temperature of approx. 900°C in the calciner.

But also other precalcining systems where kiln gases enter into contact with sufficient free CaO in the kiln riser duct and the lower cyclones absorb SO_2 from the kiln.

The only source of SO_2 emission from the preheater of a precalcining kiln system is therefore any content of non-sulfates in the raw meal which will generate SO_2 in the upper preheater stages as explained above. Many precalciner kilns in the USA have a kiln gas bypass. On leaving the kiln riser duct the kiln gas is cooled by air dilution and/or water injection to 400 to 230°C (depending on the filter system). The bypass outlet is placed to ensure the lowest possible dust concentration in the bypass gas.

This means limited possibility of absorption of the SO_2 extracted with the kiln gases in the bypass duct. Very often, more than 50% of the SO_2 contained in the by-passed kiln gases will thus enter the atmosphere via the stack. This might explain why the average SO_2 emission from the precalciner kiln systems is higher than that from the SP kiln systems.

It should be borne in mind that the evaporation factor for sulfur components in the kiln and consequently the SO_2 emission from the bypass may increase drastically if coal combustion in the precalciner is incomplete. In this case, residual carbon from the calciner will enter the kiln inlet where it will create reducing conditions, resulting in greatly increased sulfur "evaporation". Accordingly, improving the combustion in the precalciner is a mean of reducing the SO_2 emission from a system with bypass.

6. SO_2 -EMISSION REDUCTION POSSIBILITIES

To reduce the SO_2 emission from a pyroprocessing system to a certain controlled level, three basically different methods are available:

- ◆ Maintain the existing process while reducing the sulfur input into the system
- ◆ Modify the existing process (primary reduction measures)
- ◆ Maintain the existing process while adding a separate gas cleaning unit for the exhaust gas (secondary reduction measures)

6.1 Reduction of Sulfur Input into the System

Raw Material

A reduction of the total sulfur input or very important for preheater kilns the total input of sulfides is often possible. A sulfur-selective quarrying may not only reduce the total input of sulfur but also reduce its fluctuations. The maximum SO_2 retention capacity of a kiln system as described above is reached at the lowest SO_2 fluctuation. Because at very low sulfur input the absorption capacity of CaCO_3 or Ca(OH)_2 is not used completely whereas during very high sulfur input the SO_2 generation is over the absorption capacity of the raw meal. In some cases the SO_2 emission stays below limit if the sulfur content in the raw material is not fluctuating too much.

In the case of the Höver plant in Germany, the desulfurization with Ca(OH)_2 injection into the preheater is working at its limit because of its very high sulfide input. As explained below, this method is only working up to an SO_2 emission of about 1000 mg/Nm^3 dry. If Höver would not have a very homogenous sulfur content in their raw meal it would not be possible to stay below the emission limit. Not even with Ca(OH)_2 injection.

The costs of selective quarrying or opening a new quarry should be compared with the costs of the installation and operation of a system for secondary reduction measures.

A selective elimination of sulfur in the raw material is not yet developed.

Fuel

Reduction of the sulfur input via the fuel can usually only be attained by accepting a considerable increase in fuel cost. Except for the case where the fuel can be replaced by alternative fuels.

A reduction of the fuel-sulfur will under normal conditions not reduce SO_2 -emission from preheater kilns without bypass.

6.2 Modification of the Existing Process

Non-Preheater System → Preheater System

As documented and explained above, preheater systems do have the lowest SO_2 - emission of all clinker production systems.

This modification is reducing the SO_2 emission significantly if:

- ◆ the SO_2 emission is not mainly caused by non-sulfates input via the raw material
- ◆ the total input of circulating elements (S, alkali, Cl) is low enough to avoid a kiln bypass

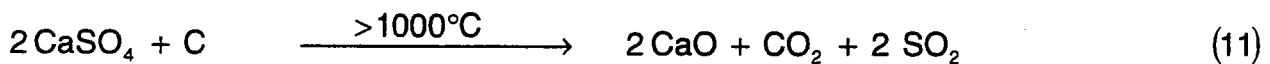
This modification is reducing the SO_2 -emission because of:

- ◆ retainment of sulfates and fuel-sulfur by embedding sulfur in the clinker
- ◆ SO_2 -adsorption during compound operation in the raw mill
- ◆ lower heat consumption

Modification of fuel preparation and feed [8]

A reducing atmosphere in the kiln is increasing the formation of CO and the volatility of " SO_2 ".

Therefore, the SO_2 emission of preheater kilns with bypass, wet and long dry kilns and to a lesser degree also of normal preheater kilns is increased if a reducing atmosphere is present in the kiln:



This can be avoided by better fuel preparation and feed as well as with an increased O_2 concentration in the kiln.

Coal, Coke:

- ◆ no oversized particles (residues on $90 \mu\text{m}$ sieve = $0,5 \times \% \text{ volatiles}$)
- ◆ continuous feed (feeder, transport)

Oil:

- ♦ good atomization: burner nozzle e.g. Pillard, Unitherm, temperature, pressure

Alternative fuels:

- ♦ solid: no oversized lumps: e.g. chipped instead of whole tires, small bundles
- ♦ liquid: see "oil" above

Besides fuel preparation and feed also the O₂ concentration in the kiln should be optimized to reduce the sulfur volatility. To control the O₂ in the kiln, a kiln inlet probe is recommended. O₂ control with gas extraction after the preheater is also possible but because of fluctuation of the false air intake into the preheater it is less accurate.

In most cases, a compromise in the O₂ concentration (reducing atmosphere) has to be found, because the NO_x-emission, fuel and power consumption can be increased by increasing the O₂-concentration in the kiln.

SO₂ adsorption in the raw mill

The exhaust gas from preheaters and long dry kilns are usually used in the raw mills to dry the raw meal. The freshly ground raw meal in the raw mill has a large and very active surface where SO₂ can be adsorbed. The highest degree of adsorption (100%) can be found at very low SO₂ concentration whereas at very high concentrations (2500 - 3000 mg/Nm³ dry) like at the Untervaz plant only an adsorption of about 30% is possible. In systems with an emission of about 1000 to 1500 mg/Nm³ dry an adsorption of 50% is normal.

The degree of adsorption in the raw mill is also influenced by the temperature and the humidity. A lower temperature or a higher humidity is increasing the adsorption capacity.

Raising the proportion of compound to direct operation, time is reducing the time of high SO₂ emission and therefore also the effort of secondary measures (e.g. amount of Ca(OH)₂ added to the kiln feed).

6.3 Secondary Reduction Measures

Catalytic or non-catalytic elimination of SO₂ (as it is known for NO_x) is not reasonable because oxidation would lead to SO₃ and reduction to SH₂, both would be more harmful than SO₂.

Therefore, only absorption or adsorption of SO₂ can be used as secondary reduction measures.

SO₂ absorption with Ca (OH)₂ (slaked lime) [9]

The most common measure against SO₂ emission is SO₂ absorption with Ca (OH)₂.



It can be added to the exhaust gas:

- ♦ at the upper cyclone stage of the preheater together with the kiln feed
- ♦ in a scrubber after the kiln system

The addition of Ca(OH)₂ to the kiln feed is very successfully used in three "Holderbank" plants with preheaters (RK, HV, UV) (see chapter 7). However, this technology has its limits. For instance only concentrations not exceeding about 1000 mg SO₂/Nm³ can be reduced. At the same time, the emission limit value should be less than 400 mg SO₂/Nm³.

at Untervaz

If the normal SO₂ emission is very high (> 1000 mg/Nm³) as it used to be in the Untervaz (UV) plant in Switzerland, a separate SO₂ scrubber after the preheater has to be considered. The only slaked lime scrubber for a cement plant was built in the UV plant. There, the kiln exhaust gas flows through a Venturi reactor with an expanded fluidized bed formed by the absorbent which consists of a blend of hydrated lime (slaked lime) and raw meal [9]. A more detailed description of the UV reactor is attached (see chapter 7).

Experience showed that the temperature for SO₂ absorption with slaked lime is very important. Efficient absorption was only observed at temperatures above 350°C and below 70°C. Therefore, systems with Ca(OH)₂ injection into the conditioning tower or Ca(OH)₂ in bagfilters do not have a sufficient SO₂ absorption efficiency [10].

Replacement of Ca(OH)₂ power by other Ca-compounds

To save on the high cost of the fine slaked lime, other desulfurization agents were tested at the Höver plant of Nordciment for their suitability. These were coarser slaked lime, powdered chalk and partly calcined kiln meal. However, the results of these experiments were mostly unsatisfactory. The effectiveness of the slaked lime currently in use was in no case anywhere near achieved. Powdered chalk has the lowest effectiveness. The reactivity of the coarse slaked lime was also barely detectable due to the small surface area. In the case of the partly calcined raw meal which had been pneumatically withdrawn from the lowest cyclone stage of a preheater, a slight desulfurization effect could be discerned. However, the technical problems in handling were so great that its further use was abandoned.

Tests with unslaked lime (CaO) were not carried out since on account of its lower reactivity compared with slaked lime, the difference in cost does not justify the increased quantities required. Optimization, e.g. also for absorption of larger quantities of SO₂, is only likely to be achieved by selecting a finer slaked lime. Thus a material with a BET specific surface of 18 or 36 m²/g could certainly lead to fixation of larger quantities of SO₂.

Untervaz started to use a Ca(OH)₂-mud from a former dump of a carbide manufacturer. The mud has a negative price and can be added to the raw material. This is reducing the Ca(OH)₂-feed to the scrubber.

At the Fort Collins plant precalcined material (CaO) from the precalciner is added to the bypass exhaust gas to reduce SO₂-emission. In addition to that, bypass dust is recirculated in the bypass to increase the concentration of SO₂ absorbed in the dust. These measures are sufficient to stay below the SO₂-limit.

Activated Coke Absorber

Activated coke is under presence of water a very efficient SO₂ absorber. The only filter of this kind is installed in the Siggenthal (SG) plant of "HCB. The SO₂ emission is reduced by the filter from above 500 to below 50 mg/Nm³.

However, this type of absorber is very pricy. The Polvitec in SG is only economical because of the contribution from the village of Zurich for burning their sewage sludge.

Sodiumbicarbonate Absorber

Obourg.

Passamaquoddy Absorber

SO₂ scrubbing is only a side effect of the Passamaquoddy scrubber. As described in chapter 7 the main purpose is to recover CKD to avoid dust dumping. The SO₂ is first absorbed by the CaO in the CKD and reacts afterwards with the alkali oxides in the CKD to form an alkali salt. The alkali salt is extracted and if possible sold as a fertiliser.

7. EXAMPLES OF SO₂ EMISSION REDUCTION

Below a collection of short descriptions of plants and their measures against SO₂ emission. Everybody is welcome to contribute to this collection.

SO₂-emission reduction

Plant:	Fort Collins (FC)
Capacity:	1500 t/d (design) / 1345 t/d (standard)
Raw material:	Containing kerogen and sulfur (~10% as Pyrite)
Fuel type:	Nat. gas, coal (0.44 % S), pet coke (4 to 5% S)
Plant description:	1-stage-preheater with precalciner
Supplier/equipment:	Polysius preheater, Allis-Chalmers kiln
Initial SO ₂ -emission problem:	The SO ₂ -limit of 150 ppm (i.e.~ 320 mg/Nm ³) can not [1], always be maintained, (sometimes up to 300 ppm) [2] and limits the kiln output. The SO ₂ emissions originate from the bypass and not from the precalciner. Kerogen in the raw material is burned in the calciner, combusted into CO ₂ and SO ₂ . At the same time CaO reacts with SO ₂ if sufficient Oxygen is available to form CaSO ₄ (SO ₂ scrubbing). The bypass is the control valve for the sulfur level in the clinker. The bypass rate is 100 %!
Solutions investigated:	[2] The reason for the emission from the bypass is believed to be due to a limited quantity of CaO being available in the bypass dust to combine with SO ₂ from the kiln. So adding some dust to the bypass-duct would help. Since a lot of sulfur input into the system is from coal, the specific fuel input has to be reduced. The sulfur content of the kiln feed is rather high with 3.6%. In order to control the SO ₂ -emission, a splitter gate should be installed, in order to deviate a portion of return dust to the bypass scrubber.
Solution realized:	[4] Dust return (mainly precalciner dust) from the bypass / precalciner bagfilter into the bypass duct has been installed before 1994, however the return dust system needs further modifications.
Emissions reached:	[3] The necessary SO ₂ -limit has been reached. Most of the time, no additional scrubber dust is used for stack sulfur control. Consequently the low stack SO ₂ (average 40 - 50 ppm) would allow a lower waste dust quantity.
Further Optimization:	[3],[4] The plant capacity should be increased up to 1600 t/d with several modifications (and reduction of losses), without increasing the emissions. A modification of the kiln feed inlet is planned for 1995.

Literature:

REFUT OPERATIONS - 12th CTB

SO₂-emission reduction

Plant:	Höver (HV)
Capacity:	3'000 t/d (design), 2'900 t/d (standard)
Raw material:	Sulfur components: Pyrite 0.05 - 0.45 %w/w
Fuel type:	Coal (0.4%S), fuel oil, nat. gas; alternative fuels: whole tires (max. 10% of total heat input)
Plant description:	Kiln with 4-stage twin line suspension preheater and planetary cooler
Supplier/equipment:	KHD kiln and preheater
Initial SO ₂ -emission problem:	SO ₂ emissions of up to 1300 mg/Nm ³ [1],[2] (TA Luft = 400 mg/Nm ³) In direct operation, up to 900 mg/Nm ³ in compound operation
Solutions investigated:	The following investigations were proposed: [3],[4],[5] Reduction of SO ₂ emissions by lowering the exhaust gas temperature. Lowering the temperature in the raw mill in compound operation. Desulfurization with Ca(OH) ₂ : different trials have been carried out. To reach an emission < 400 mg/Nm ³ , the SO ₂ concentration in the stack should be held at about 350 mg/Nm ³ . The calculated amount (based on trial results) of Ca(OH) ₂ needed to stay below the limit would have been 2.4 kg/t clinker in 1990 and 6.4 kg/t clinker in 1991.
Solution realized:	Desulfurization with Ca(OH) ₂ addition to the kiln feed (bucket elevator). The Ca(OH) ₂ is proportioned by speed control rotary valves with three independent pneumatic injection pipes, which can be used simultaneously when required. The Ca(OH) ₂ addition was started up in November 1991.
Emissions reached:	[1] The addition of Ca(OH) ₂ is controlled by the measured SO ₂ -concentration at the stack, in order to stay below the TA-Luft limit of 400 mg/Nm ³ .
Further Optimization:	[1] Since the costs for slaked lime are quite high, different other desulfurization agents have been tested: powdered chalk: low absorption efficiency coarse slaked lime: barely detectable effect due to small surface area partly calcined raw meal: slight desulfurization effect, but additional technical problems. Tests with unslaked lime (CaO) have not been carried out, due to its low reactivity compared with Ca(OH) ₂ . A further optimisation could be reached, using a finer slaked lime (higher surface area).

Literature:

- [1] Boes, K.-H.: Measures to reduce the SO₂ emission during clinker burning at Nordciment AG's Höver works.
Zement, Kalk, Gips (1993), P.514-518
- [2] Waltisberg, J.: HMB Aktennotiz VA 86/66/D,
VA-Dok: HV, Reg. 17
- [3] Hasler, R.: HMB letter to Nordciment AG,
VA-Dok: HV, Reg. 17
- [4] Waltisberg, J.: HMB Bericht VA 87/5437/D,
VA-Dok: HV, Reg.18
- [5] Waltisberg, J.: HMB Bericht VA 91/5904/D,
VA-Dok: HV, Reg. 1

Figure A Slaked lime chemical and physical data [1]

**"Blütenweiss slaked white lime from Fels-Werke GmbH
Chemical and physical data**

CaO	71.99%
MgO	0.65%
SiO ₂	2.00%
Fe ₂ O ₃	0.45%
Al ₂ O ₃	0.47%
SO ₃	0.27%
CO ₂	1.23%
Combined H ₂ O	21.60%
Moisture	0.90%
BET	approx. 10 m ² /g
Ca(OH) ₂	90.0%

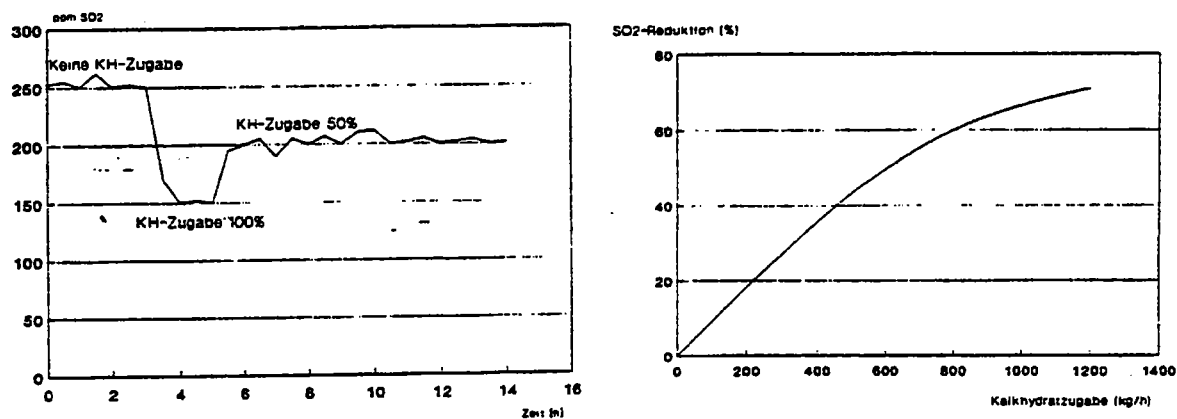
Fineness:
R > 0.063 mm 4.0%

"Blütenweiss slaked white lime from Fels-Werke GmbH

Chemical and physical data

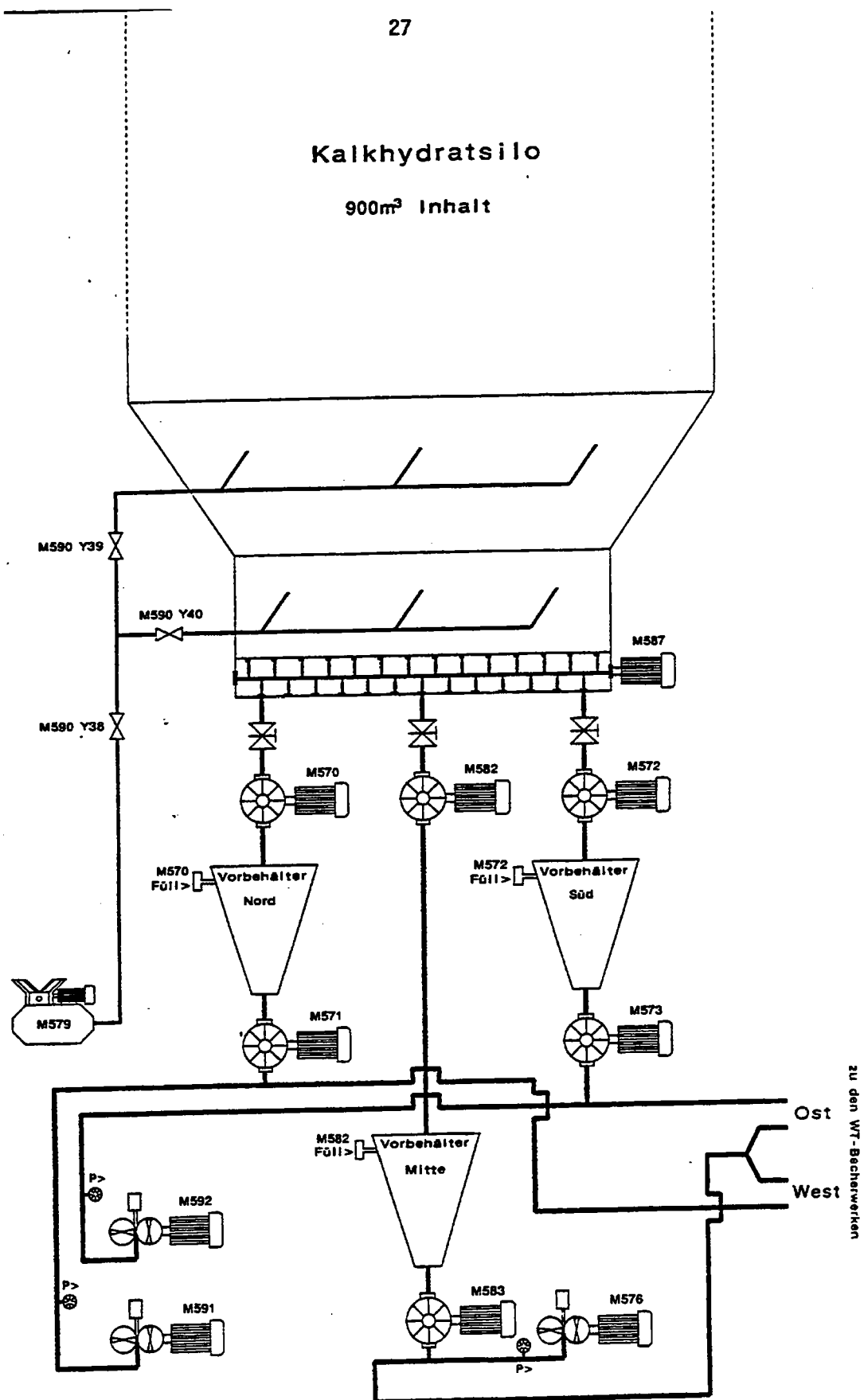
CaO	71.99%
MgO	0.65%
SiO ₂	2.00%
Fe ₂ O ₃	0.45%
Al ₂ O ₃	0.47%
SO ₃	0.27%
CO ₂	1.23%
Combined H ₂ O	21.60%
Moisture	0.90%
BET	approx. 10 m ² /g
Ca(OH) ₂	90.0%
Fineness:	
R > 0.063 mm	4.0%

Figure B SO₂ reduction efficiency with slaked lime addition



Keine KH-Zugabe	=	no slaked lime feed
KH-Zugabe	=	slaked lime feed
Zeit	=	time
SO ₂ -Reduktion	=	SO ₂ reduction
Kalkhydratzugabe	=	slaked lime feed rate

Figure C Slaked lime silo and dosing



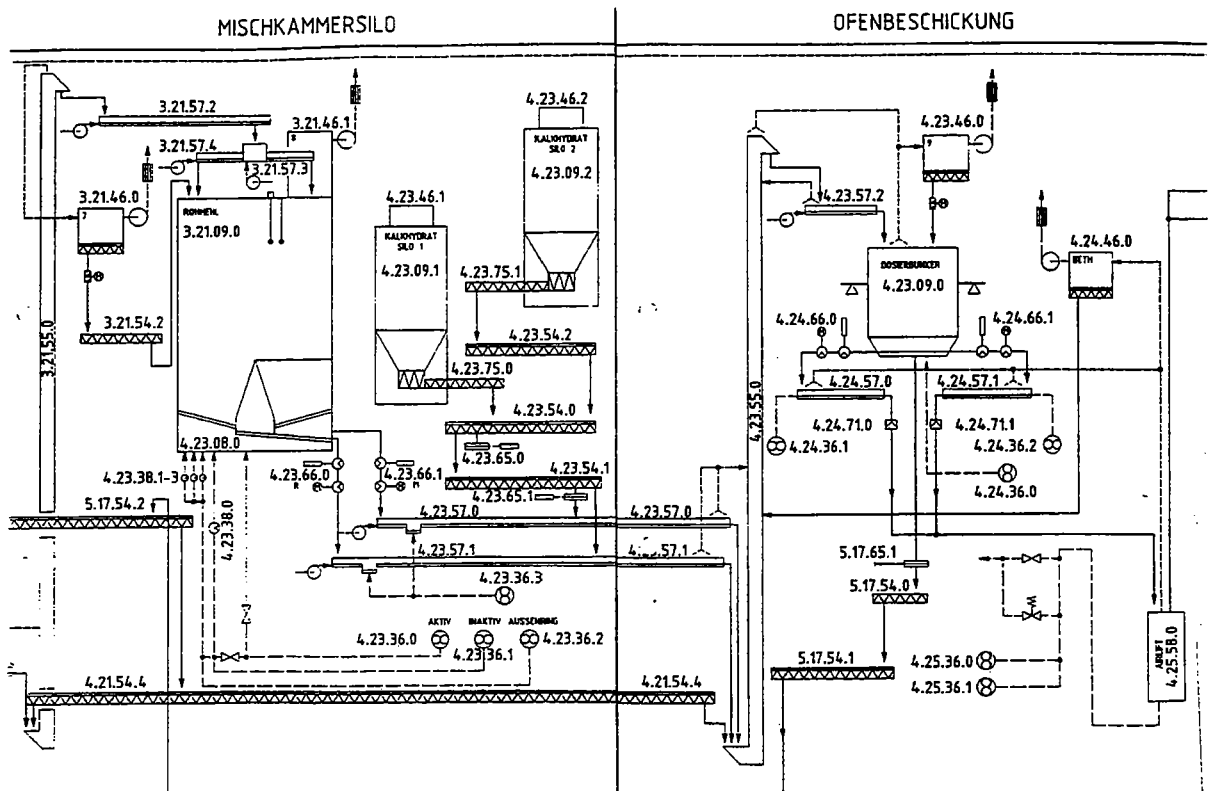
SO₂-emission reduction

Plant:	Rekingen (RK)
Capacity:	2'200 mtpd (design), 2130 mtpd (standard)
Raw material:	Sulfur component: 0.55 % Pyrite
Fuel type:	Coal 0.4%S, fuel oil 0.8%S, waste timber
Plant description:	4-stage-suspension preheater kiln
Supplier/equipment:	Polysius kiln and preheater
Initial SO ₂ -emission problem:	SO ₂ emissions of up to 1200 mg/Nm ³ (LRV-limit = 500 mg/Nm ³) in direct operation [LRV = Swiss clean air act]
Solutions investigated:	Reduction of SO ₂ emissions by lowering the exhaust gas [1],[2] temperature. Reduction from 180°C to 150°C results in a reduction of 50 mg/Nm ³ , the same reduction is obtained by further lowering the temperature to 140°C. Desulphurization with Ca(OH) ₂ , added to the kiln feed only during direct operation leads to a reduction of 400 - 450 mg/Nm ³ at an initial emission of 750 - 1200 mg/Nm ³
Solution realized:	[3] Desulphurization with Ca(OH) ₂ addition to the kiln feed 3 kg/tcli (max. 17kg/tcli) during direct operation (20% of the operating time) Costs are about 60'000 CHF/year
Emissions reached:	The addition of Ca(OH) ₂ is controlled by measuring the SO ₂ concentration in the stack, in order to reach the limiting values of LRV, i.e. below 500 mg/m ³ .

Literature:

- [1] Utzinger, K.: Reduktion der SO₂-Emissionen durch Senkung der Abgastemperatur, Versuchsbericht (1986), VA Dok: RK, Reg.17
- [2] Scheuch, J.: Entschwefelungsversuche mit Ca(OH)₂ im Ofendirektbetrieb, Versuchsbericht (1986), VA Dok: RK, Reg.17
- [3] "Holderbank" Cement Course: Source and reduction of emissions gaseous, VA 91/5882/E, P.7

Figure A Dosing of slaked lime to the kiln feed

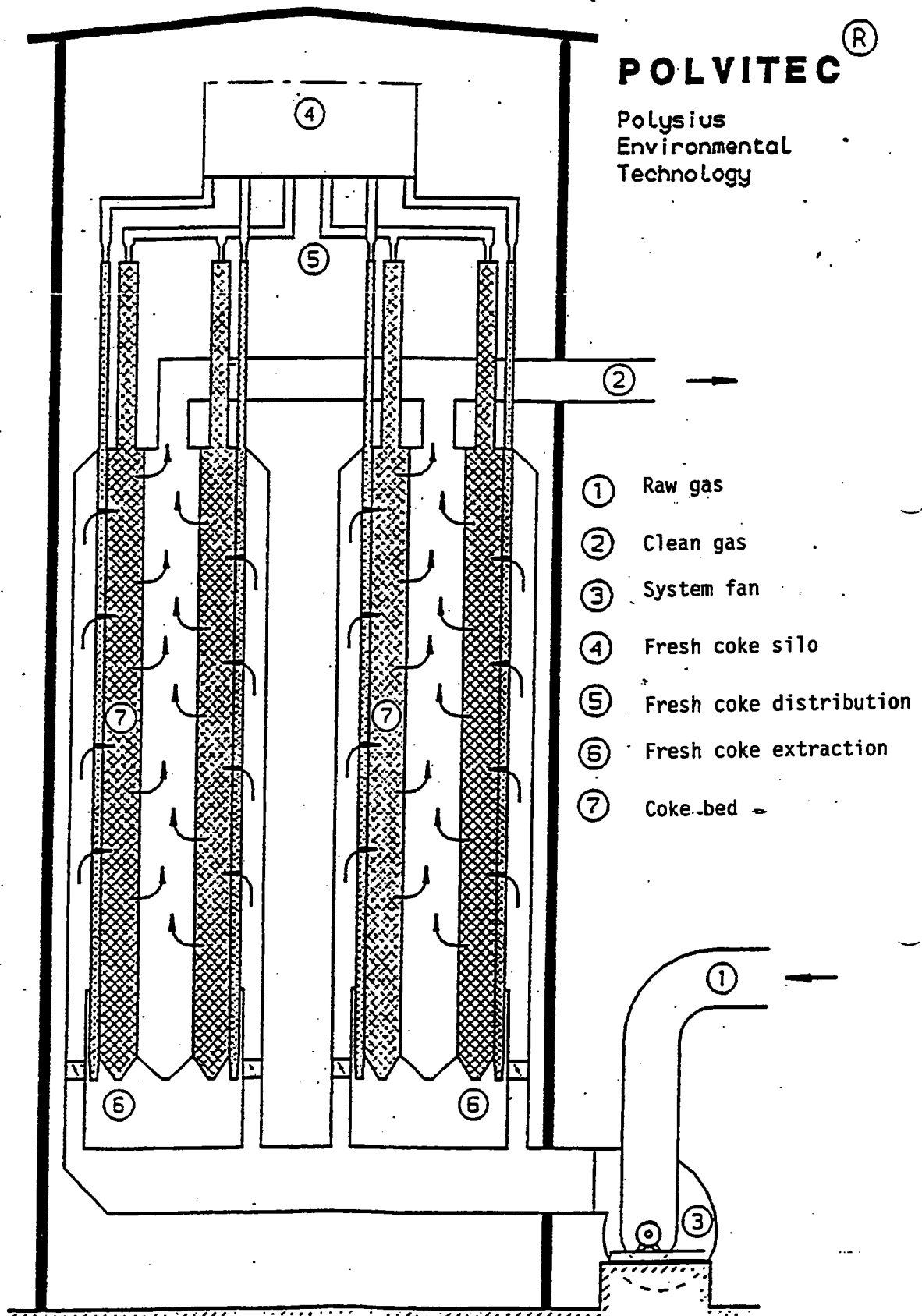


SO₂ -emission reduction

Plant:	Siggenthal (SG)
Capacity:	2000 t/d (design), 1900 t/d (standard)
Raw material:	[2] Sulfur: 0.7% S
Fuel type:	[2] Fuel oil (2.3%S), dried sewage sludge, complete tires (1.3%S)
Plant description:	Kiln with 4-stage preheater
Supplier/equipment:	Polysius kiln and preheater (Dopol), Fuller grate cooler
Initial SO ₂ emission problem:	SO ₂ emissions of up to 1500 mg/Nm ³ in direct operation, [1] up to 900 mg/Nm ³ in compound operation (LRV-limit = 500 mg/Nm ³) [LRV = Swiss clean air act]
Solutions investigated:	SG had a project to burn sewage sludge containing Hg and at the same time the SO ₂ and NO _x emissions where too high. A pilot plant with an active coke filter as well as an ammonia injection into the riser duct was tested successfully. Mercury, SO ₂ and other pollutants were absorbed on the active coke. NO _x was reduced to N ₂ and H ₂ O with ammonia injection.
Solution realized:	A POLVITEC (Polysius Environmental Technology) active coke scrubber behind the kiln EP was successfully commissioned in 1994. Beside SO ₂ and Mercury it is also filtering out other pollutants like heavy metals, NH ₃ , organic compounds and dust. The loaded coke is injected into the kiln as a fuel substitution. Investment cost: 30'000'000 CHF Operating cost: 3.3 CHF/t cli Emissions reached: [3] < 12 mg/Nm ³ dry

Literature:

- [1] Dr. R. Stenger, : HMB Bericht MA 92/93/D, VA Dok: SG, Reg. 2
- [2] ATR, Annual Technical Report 1994, "Holderbank"
- [3] Effektive Emissionsminderung bei Einsatz von Sekundärbrennstoffen im Zementdrehofen von "HCB Siggenthal, Dr. 1§D. Rose, Dr. L. Brentrup, Krupp Polysius



SO₂-emission reduction

Plant:	Untervaz (UV)
Capacity:	1900 t/d (standard)
Raw material:	Sulfur components: Pyrite and Markasit, usually 10 - 16 g SO ₃ /kg clinker
Fuel type: [7]	Coal (0.07%S), fuel oil; alternative fuels as dried sewage sludge, waste oil (0.6%S), distillation residue (0.35%S), plastic (0.02%)
Plant description:	Kiln with 4-stage-suspension preheater and planetary cooler (kiln III)
Supplier/equipment:	KHD kiln, preheater and cooler; Lurgi SO ₂ -scrubber
Initial SO ₂ -emission problem:	SO ₂ emissions of up to 3600 mg/m ³ (LRV-limit = 500 mg/Nm ³) in direct operation [LRV = Swiss clean air act]
Solutions investigated:	<p>In 1984/85 trials to lower the SO₂ emissions by changing</p> <p>[1],[2],[3],[4] the operating parameters have been carried out. Addition of Ca(OH)₂ to the raw meal: Reduction of up to 50% of SO₂, still insufficient.</p> <p>Because no possibility of lowering the SO₂ emission of the Plant to the required 500 mg/Nm³ by simple means as the one explained above could be found, the use of a scrubber had to be considered. Because a wet SO₂ absorber (washer) was too expensive (investment and operating costs) a dry absorber was chosen.</p>
Solution realized:	<p>A system consisting of a circulating fluidized bed supplied</p> <p>[1],[2] by Lurgi, Germany, was started up in 1988. It works as follows:</p> <p>The kiln exhaust gas flow through a venturi reactor with an expanded fluidized bed formed by the absorbent that consists of a blend of hydrated lime (93% Ca(OH)₂) and raw meal (0.8-1.0t/h Ca(OH)₂ and 2.5t/h raw meal). The latter is mainly added to prevent caking of the very fine hydrated lime. Water is injected to operate the reactor as close as possible to the water dew point and to promote the reaction with the SO₂. Due to the intensive contact of the exhaust gas with the absorbent in the fluidized bed at a temperature (approx. 65°C) close to the water dew point (approx. 58 to 61°C), the SO₂ becomes very effectively combined with the absorbent, whereby predominately calcium sulfite (CaSO₃) is generated. The absorbent then passes with the exhaust gas into an electrostatic precipitator. The bulk of the precipitated absorbent is returned to the venturi reactor (approx. 175t/h), while the remainder is discharged and either returned to the kiln feed or added to the cement. The stoichiometric factor of Ca(OH)₂ to SO₂ is about 2.3 to 2.6.</p> <p>The pressure loss in the system is 2200 Pa. This results</p>

in a power demand for the fan of 315 kW. With the addition of 155 kW for the electrostatic precipitator and the transport systems, the total power consumption of the system amounts to 470 kW.

Adding all the material to the kiln feed results in an increase of the SO₃ content in the clinker from 1.0 to 1.3%. This is not desirable, but so far not of much concern, because it has turned out that the additional sulfates in the clinker act as a gypsum substitute, so that the SO₃ content of the cement can be kept at 2.7% SO₃ as before.

The investment for the whole desulfurization plant, including auxiliary installations, amount to 15 million CHF. The operating costs are about 2.2 CHF/t cli (Slaked lime 1.6, electrical power 0.4, maintenance 0.5, gypsum substitution 0.3 CHF/t cli).

Emissions reached: [5]

During the acceptance measurements in May 1989, the following values have been reached:

Direct operation: 431 mg/m³

Compound operation: 418 mg/m³

Further Optimization: [6]

In 1990 the circulating fluidized bed was operated with 1 t/h hydr. lime and 2.5 t/h raw meal. It has been investigated to use hot meal instead of hydr. lime. Due to analyses of hot meal, it seemed not to be possible to replace hydr. lime completely, but it should be tested whether a part of the hydr. lime could be replaced

Literature:

- [1] Bonn, W., Hasler, R.: Verfahren und Erfahrung einer roh- stoffbedingten SO₂-Emission im Werk Untervaz der Bündner Cementwerke. Zement, Kalk, Gips (1990), P. 139-143
- [2] "Holderbank" Cement Course: Source and reduction of emissions gaseous, VA 91/5882/E, P. 5 - 6
- [3] Hasler, R., Wickert, Dr.H.: HMB Bericht VA 86/5281/D, VA-Dok: UV, Reg. 17A
- [4] Berclaz, Ch.:HMB Bericht VA 85/73/D, VA-Dok: UV, Reg. 17A
- [5] Strahm, E., Waltisberg, J.: HMB Bericht VA 89/5665/D, VA-Dok: UV, Reg. 2
- [6] Waltisberg, J.: HMB Aktennotiz VA 90/6/D, VA-Dok: UV, Reg. 2
- [7] ATR, Annual Technical Report 1994,"Holderbank"

Figure A Burning of dried sewage sludge in a cement kiln

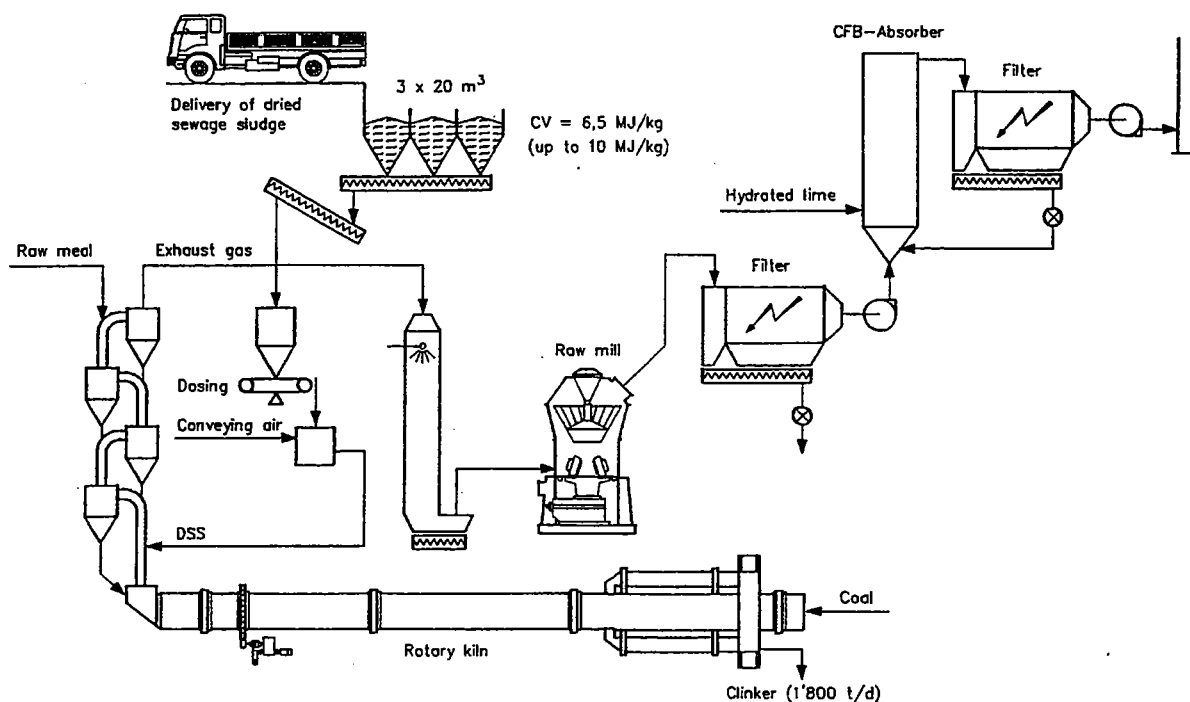
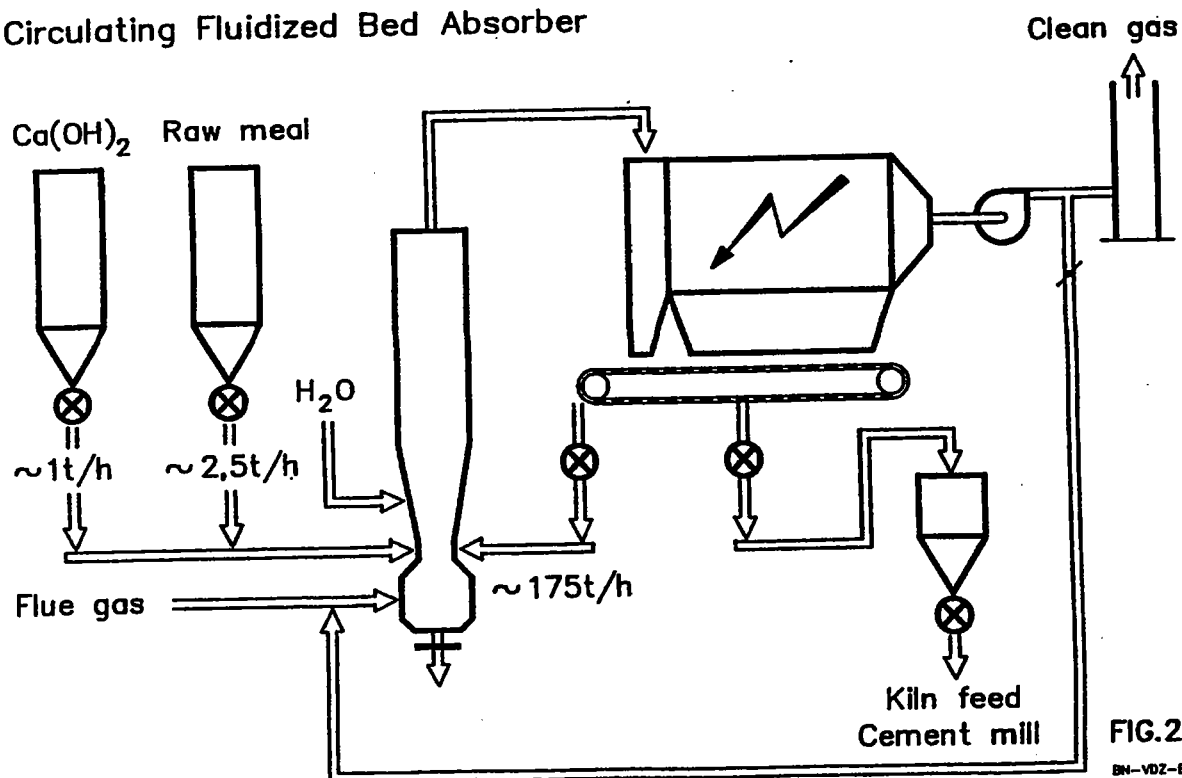


Figure B Circulating Fluidized Bed Absorber

Circulating Fluidized Bed Absorber



SO₂-emission reduction

Plant:	Aalborg Portland (not in Holderbank Group)
Capacity:	0.5 Mio. t/year of white clinker with 4 kilns
Raw material:	
Fuel type:	Fuel oil and pet coke
Plant description:	Wet process plant
Supplier/equipment:	FLS
Initial SO ₂ emission problem:	Due to the white color of white clinker, and since in the
	[1] white kilns very little sulfur is retained, only special fuel quality could be used. Most of the sulfur was emitted as SO ₂ in concentrations of 500 - 800 ppm.
Solutions investigated:	<p>Since the fuel consumption is generally higher for white clinker and for a wet process, in 1980 a conversion to a semi-wet process was considered. Due to high capital costs and technical risks this investigation was not followed further.</p> <p>The recovery of some of the waste heat seemed to be a more attractive solution. In combination with the SO₂-problem, a combined heat recovery and desulfurization process seemed to be very attractive, and it was decided to build a pilot plant. From March 1989 to February 1990 a test program was carried out. The degree of desulfurization was found to be 75 %.</p>
Solution realized:	<p>The heat recovery and SO₂ absorption unit for the four wet kilns consisting of 4 gas/water heat exchangers and 2 scrubber systems was commissioned in 1991.</p> <p>The exhaust gas from the kiln passes first the gas/water heat exchanger before it enters the SO₂ scrubber at a temperature of about 115°C. In the scrubber SO₂ is absorbed in a slurry loaded with 6 10% solids consisting of 98% CaSO₄·2H₂O and 2% CaCO₃. The slurry is sprayed in counter current to the exhaust gas and collected in the recycle tank at the bottom of the scrubber where it is oxidized with air ($\text{CaSO}_3 + 0.5\text{O}_2 \rightarrow \text{CaSO}_4$). A part of the slurry is pumped to a centrifuge where water and gypsum are separated. The rest is reinjected through a circulation line into the scrubber. A chalk slurry of 30% moisture is injected into the circulation line before the spray nozzles to replace the used and extracted absorbens ($\text{CaCO}_3 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{CO}_2$). The optimum pH for the circulated slurry has been found to be between 5.4 and 5.6 and is controlled by the amount of chalk slurry added to it.</p> <p>The circulated slurry passes on its way from the recycle tank to the nozzles a heat exchanger to</p>

preheat the water for the gas/water heat exchanger.

The exhaust gas leaves the scrubber with 75% less SO₂ and a temperature of about 70°C.

Emissions reached:

The scrubber reaches an SO₂ reduction of 75-80%, i.e. the remaining SO₂-concentration is below 160 200 ppm.

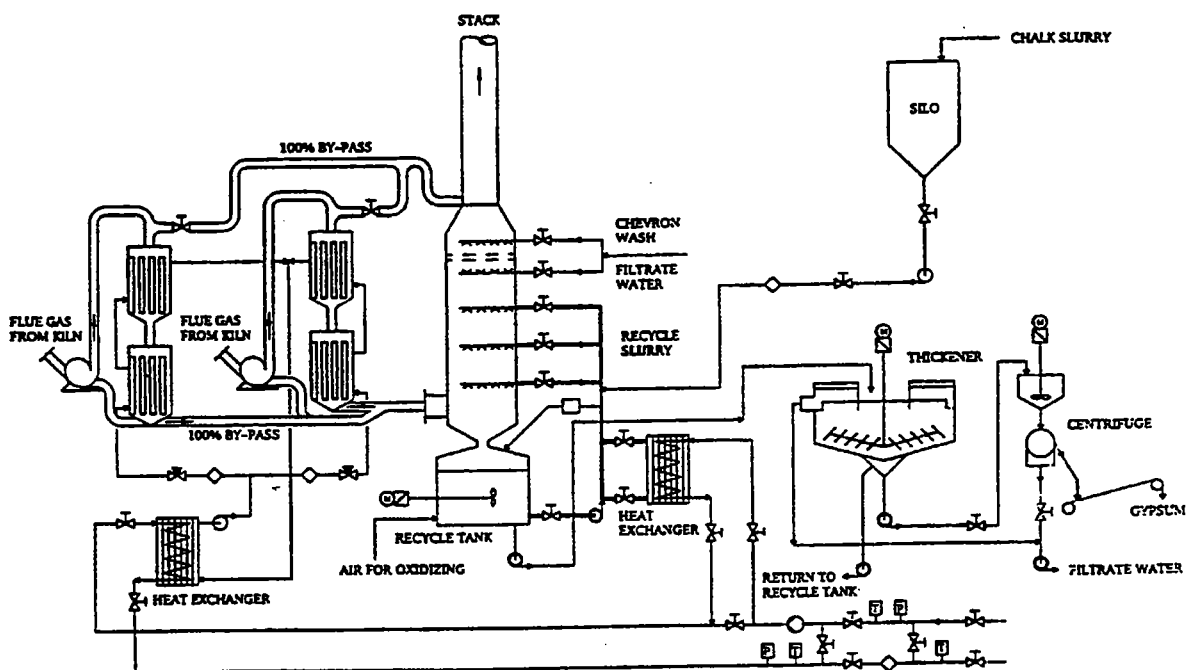
Further Optimization:

Further optimization concerning the desulfurization is not foreseen.

Literature:

- [1] H.E.Borgholm: A new heat recovery and desulfurization plant for 4 wet kilns in Aalborg Portland. 35th IEEE cement industry technical conference in Toronto, IEEE catalogue (1993), 395 - 409.

Figure A Heat recovery and desulfurization plant of Aalborg Portland / Denmark



SO₂-emission reduction

Plant:		Dragon Products, Thomaston (Maine, USA), (not in "Holderbank" group)
Capacity:	[1]	4000'000 t/year
Raw material:		
Fuel type:		
Plant description:		Wet kiln
Supplier/equipment:		
Initial SO ₂ emission problem:		SO ₂ emissions never were a problem (500 mg/Nm ³).
	[1]	During the time when Martin Marietta owned the plant (i.e., before 1980), the US EPA designed Thomaston, an upper class coastal residential area, a non attainment area (i.e. an area which had not attained the required level of emissions). This was due to dust emissions from both kiln and quarry (CKD). The Dragon plant discarded dust to produce a lower, but not a low alkali cement.
Solutions investigated:		
Solution realized:	[1],[2]	<p>The Passamaquoddy scrubber was commissioned in 1990. Conversion is accomplished in the Recovery Scrubber by reintroducing into CKD the CO₂ that was released during calcining. Exhaust gas from the kiln is cooled in a heat exchanger (A) and bubbled through a reaction tank (B) containing a slurry of CKD and water. CO₂ in the gas reacts with CKD in the slurry to reclaim CKD for kiln feed, while SO₂ reacts with potassium sulfate in the CKD to form potassium sulfate in solution.</p> <p>$\text{CaO} + \text{SO}_2 + 0.5\text{O}_2 \rightarrow \text{CaSO}_4$$\text{CaSO}_4 + 2\text{KOH} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$</p> <p>Reclaimed CKD is separated in a settling tank (C), rinsed in a secondary settling tank (D) to remove potassium sulfate remnants, and returned to the cement plant as raw feed. Potassium solution is pumped to the crystallizer (E) for recovery as dry potassium sulfate. Heat for the crystallizer is obtained from the exhaust gas heat exchanger (F).</p>
Emissions reached:	[3]	The exhaust gas SO ₂ elimination is claimed to be over 90%. Beside SO ₂ also HCl as well as ammonia and some less volatile organic compounds are absorbed.

8. LITERATURE

- [1] Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 25, 1994 VCH, 3-527-20125-4
- [2] Handbook of Chemistry and Physics, 60th Edition, CRC-Press, 0-8493-0460-8
- [3] Säurehaltige Niederschläge - Entstehung und Wirkung auf terrestrische Ökosysteme, 1984, VDI, Kommission Reinhaltung der Luft
- [4] F.L. Smidth, An overview of the formation of SO_x and NO_x in various pyroprocessing systems; P.B. Nielsen, O.L. Jepsen, No. 96
- [5] Der Anteil der Zementindustrie an den anthropogenen SO₂- und NO_x-Emissionen, H. Wickert, "Holderbank" News 6, 1985, p. 15-16
- [6] ATR-Databank 1994
- [7] Kiln Optimization Seminar, Circulation Phenomena VA 90/5714/E, U. Gasser
- [8] Kiln Optimization Seminar, Fuel Preparation / Firing Systems, VA 89/5653/E, F. Schneider
- [9] Environmental Protection Seminar, Sources Reduction of Emissions (gaseous), VA 91/5882/E, J. Waltisberg
- [10] Parameter study on desulfurization in baghouse filter, VA 90/5687/E, A. Edlinger, R. Hasler
- [11] Massnahmen zur Minderung der SO₂-Emission beim Klinkerbrennen im Werk Höver der Nordciment AG, K.H. Boes
- [12] Emissions of NO_x and SO₂ from cement clinker burning, V. Johansen, A.H. Egelov, Denmark

Figure 14 SO_2 -Reduction = f(Mol-ratio Ca/S)

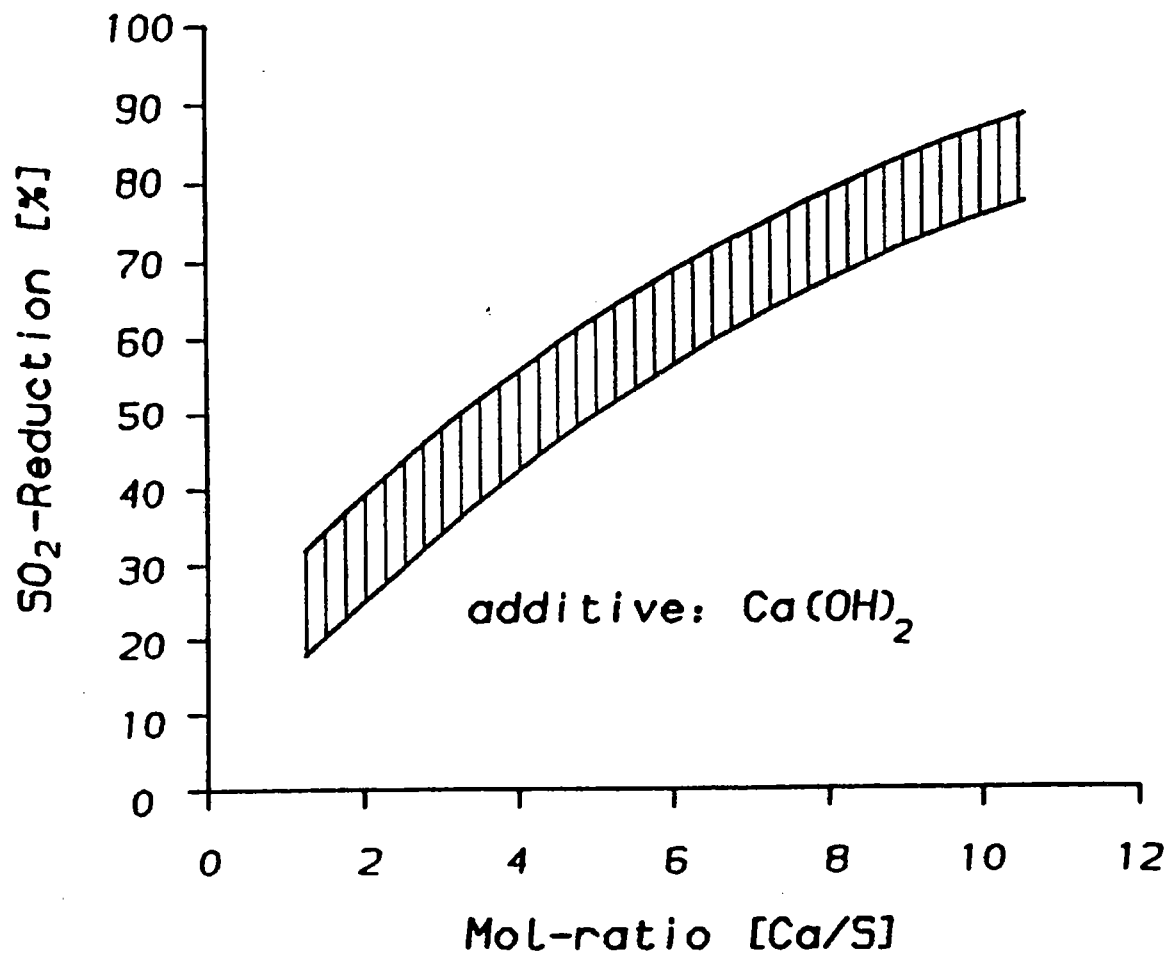


Figure 15 SO_2 REDUCTION WITH $\text{Ca}(\text{OH})_2$

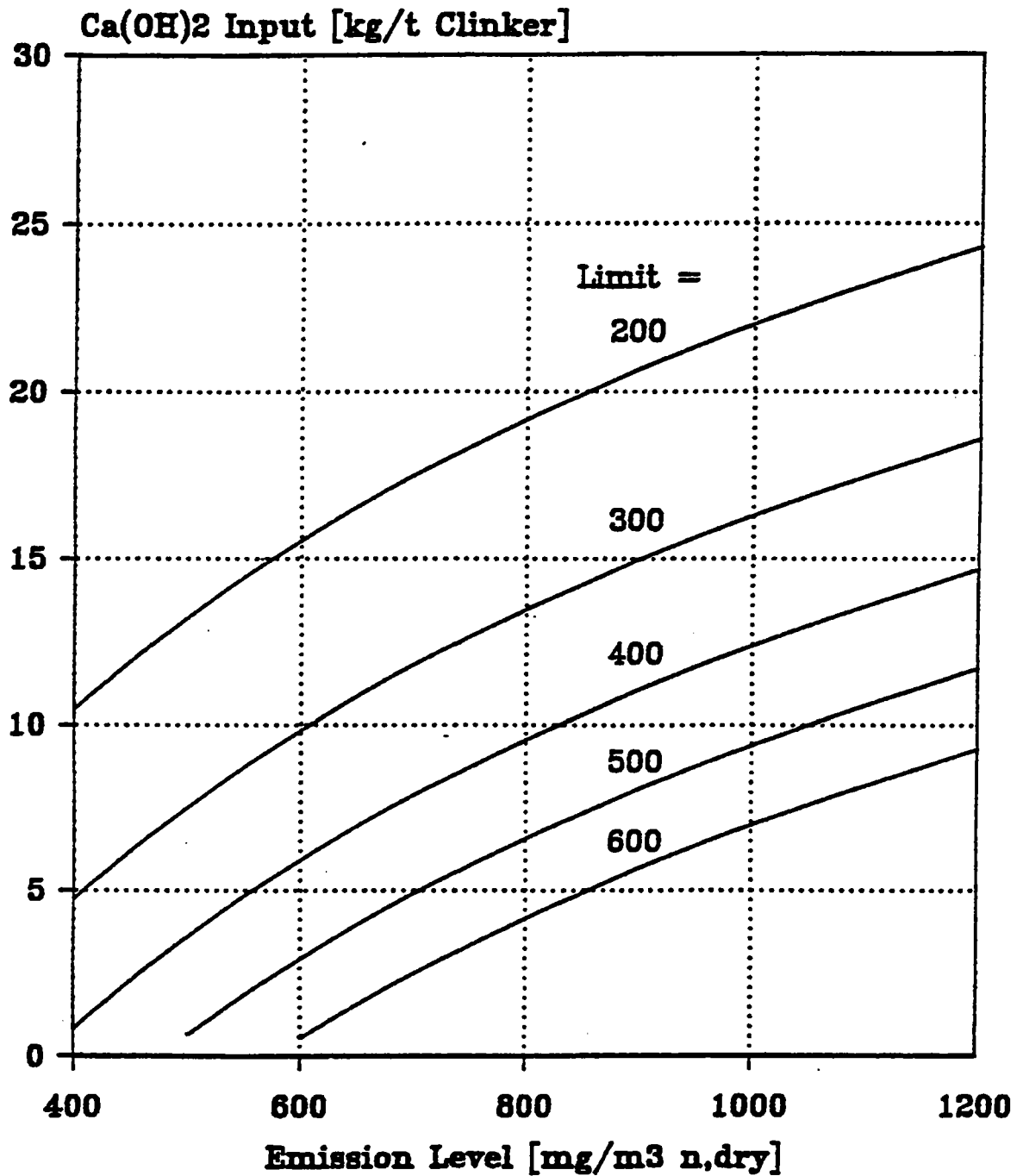


Figure 16 Influence of oxygen content in the kiln gas

